ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

OXIDATIVE CROSS-DEHYDROGENATIVE COUPLING OF TERMINAL ALKYNES WITH THIOLS USING Cu(I) INCORPORATED SCHIFF BASE NETWORK POLYMER AS CATALYST

M.Sc. THESIS

Yonca ALKAN

Department of Chemistry

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

UÇ ALKİNLER İLE TİYOLLERİN Cu(I) BAĞLANMIŞ SCHIFF BAZ AĞ POLİMERİ KATALİZÖRÜ EŞLİĞİNDE OKSİDATİF ÇAPRAZ DEHİDROJENATİF BİRLEŞTİRME REAKSİYONLARI

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ARALIK 2015

Yonca ALKAN, a M.Sc. student of ITU Graduate School of Science Engineering and Technology 509141031 successfully defended the thesis entitled **"OXIDATIVE CROSS-DEHYDROGENATIVE COUPLING OF TERMINAL ALKYNES WITH THIOLS USING Cu(I) INCORPORATED SCHIFF BASE NETWORK POLYMER AS CATALYST"**, which he/she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : **27 Kasım 2015**
Date of Defense : **22 December 2015**

To my family and friends,

FOREWORD

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December 2015

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(Chemist)

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ABBREVIATIONS

^{1}H NMR	**:** Hydrogen Nuclear Magnetic Resonance Spectroscopy
^{13}C NMR	**:** Carbon Nuclear Magnetic Resonance Spectroscopy
FT-IR	**:** Fourier Transform Infrared Spectrophotometer
GPC	**:** Gel Permeation Chromatography
DCM	**:** Dichloromethane
$CDCl_3$	**:** Deuterated Chloroform
THF	**:** Tetrahydrofuran
DMF	**:** N,N-Dimethylformamide
DMSO	**:** Dimethyl Sulfoxide
CuBr	**:** Copper (I) Bromide
SNW	**:** Schiff Base Network Polymer
CDC	**:** Cross-Dehydrogenative Coupling
TBHF	**:** *tert*-Butyl Hydroperoxide

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SUMMARY

Alkynes are an important class of organic molecules because of their versatile applications in materials science and organic synthesis as building blocks. Sulfur-containing compounds have also a crucial role in synthetic organic chemistry since sulfur moiety acts as an important auxilary functional group. There has been an effort to combine these alkynes with sulfur-containing compounds by using metal-acetylides and sulfuryl halides or disulfides. However, these methods require a prefunctionalization progress of terminal alkyne or sulfur-containing coupling partners. This situation causes large number of side product formations which results in a dramatic decrease in the yields of reactions. Hence, the discovery of a new method to perform these reactions in high yields and better conditions gains a considerable attention. There are lots of studies on designing an useful catalyst to remove prefunctionalization processes and provide high yields and resusability.

The term "catalysis" was first employed by Bezelius in 1836 tı şdentify a new entity capable of promoting the occurrence of a chemical reaction by a "catalytic contact". In his view, the catalyst was seen as something that is added to the reaction to speed up the rate of the reactin (catalytic force) without being consumed or produced in the process. It is important to recognize that the catalysis can be traced back to the ancient terms. However, catalysis started to play a major impact on the chemical industry starting from the begining of twentieth century, nowadays more than 95 percent of chemicals being produced via a process that is at least includes at least one catalytic step.

Traditionally, catalysts were distinguished into homogeneous and heterogeneous; subsequently, heterogenized catalysts were also introduced. This distinction is linked to the fact that the catalyst operates respectively in the same phase where the reaction occurs (homogenous catalysts) or in a different phase (heterogeneous or heterogenized catalysts). The main difference between a homogenous and heterogeneous catalyst is the fact that in case of homogeneous catalysts, every single catalytic entity can act as a single active site. This makes homogeneous catalysts more active and selective compared to traditional heterogeneous catalysts such as oxides or supported metal particles. A major drawback of the homogeneous catalysts is the difficulty of their recovery from the reaction medium. Precipitation with subsequent recovery or distillation of the reaction products, which is an energy intensie process, are typically needed in order to re-utilize homogeneous catalysts. Such operations may often deactivate the catalyst.

Despite of these considerable advances, the problem with the homogeneous catalysis still remains to be unsolved. It is difficult to seperate catalyst from reaction mixture and reuse it. In contrast, design of an heteregenous catalysis should take increasingly more attention due to its possible advantages such as reusability, waste minimization derived from reaction workup and help to the development of green chemistry concept.

Zhao et al. reported application of a hexagonally-ordered mesoporous material (MCM-41) supported bidentate nitrogen copper(I) complex [MCM-41-2N-CuCl] as a highly efficient and recyclable copper catalyst for the direct oxidative cross-dehydrogenative coupling of terminal alkynes with thiols using O_2 as the sole oxidant under mild conditions to selectively afford a variety of alkynyl sulfides in good to excellent yields. According to their results, mesoporous material (MCM-41) has a extremely high surface area, large and uniform pore size, bidentate nitrogen copper complex can be easily formed and this complex can catalyze the coupling reaction between an alkyne and a thiol.

In this thesis, the copper(I) incorporated microporous polymers' catalytic activity towards thiol-alkyne oxidative cross-dehydrogentavie coupling reactions without any prefunctionalization process was studied.

In the first part of the thesis, the microporous network polymer was synthesized by melamine and terephtalaldehyde monomers through Schiff base chemistry. As known, the porous nature comes from the unique properities of monomers and frame of the polymer. In general, microporous organic polymers includes functional polar pendant groups such as amines, phenols or carboxylic acids since these groups can coordinate with metals. The rigid frame is also important for a ordered microporous structure. For that reason, aromatic conjugated structures or kinked aromatic high-performance polymers are used to have a rigid frame. Our choice of melamine and terephtalaldehyde as monomers is compatible with these criteria. Afterwards, the copper ions were incorporated into this microporous polymers and these materials were characterized.

In the second part of the thesis, copper incorporated microporous Schiff base network polymer was used as a catalyst in the alkyne-thiol oxidative cross-dehydrogenative coupling reactions. The spectral and molecular weight analyses were applied to characterize the products.

UÇ ALKİNLER İLE TİYOLLERİN Cu(I) BAĞLANMIŞ SCHIFF BAZ AĞ POLİMERİ KATALİZÖRÜ EŞLİĞİNDE OKSİDATİF ÇAPRAZ DEHİDROJENATİF BİRLEŞTİRME REAKSİYONLARI

ÖZET

Alkinler malzeme biliminde ve organik sentezlerde temel yapı elemanı olmalarından ötürü önemli bir yere sahiptirler. Aynı zamanda, sülfür içeren bileşikler de, sülfürün önemli bir fonksiyonel grup olmasından ötürü, sentetik organik kimyada büyük bir yere sahiptir. Bu iki önemli organik grubu birleştirebilmek için metal-asetilylidler, sülfür halitler ve disülfitler ile çalışılmıştır. Ancak bu yöntemler terminal alkin ve sülfür içeren partnerlerin önceden fonksiyonlanmalarını gerektirmektedir. Bu durum yan ürün oluşumuna ve sonuç olarak da düşük verimlere sebep olmaktadır. Ağır reaksiyon şartları, düşük kimyasal seçicilik, sınırlı sübstratlar da bu konuda karşılaşılan diğer problemlerdir. Bu sebeple, alkin bileşikleri ile sülfür içeren bileşikleri birbirine bağlamak için yüksek verim sağlayan daha ılımlı reaksiyon koşullarının araştırılması önem kazanmıştır. Ön fonksiyonlandırma olmadan, yüksek verimle reaksiyonları gerçekleştirebilmek için bir çok katalizör dizeynı çalışması bulunmaktadır.

Katalizör terimi ilk defa 1836 yılında Bezelius tarafından katalitik bir temas ile bir kimyasal reaksiyonun oluşumunu hızlandırma kabiliyetine sahip molekülleri tanımlamak amacıyla kullanılmıştır. Bu tanıma göre, katalizörler reaksiyonlarda hızı arttırmak için eklenen ve reaksyion sonunda aynı şekilde elde edilebilen moleküllerdir. Katalizörler çok eski çağlardan beri kullanılmaktadır. Ancak, 20. yüzyılın başlarında kimyasal endüstride yoğun olarak kullanılmaya başlanmıştır. Günümüzde üretilen kimyasalların yüzde 95'inin üretiminde en azından bir basamağında bir katalizör kullanılmaktadır.

Genel olarak katalizörler homojen ve heterojen olmak üzere iki gruba ayrılırlar. Eğer ki katalizör, reaksiyon ile aynı fazda ise bunlara homojen katalizörler; eğer ki katalizör, reaksiyon ile farklı fazda ise bunlara heterojen katalizörler ismi verilir. Bu iki katalizör tipi arasındaki en önemli fark, homojen katalizörlerde reaktanlar ve katalizör arasındaki temas daha fazla olmasıdır. Bu durum homojen katalizörleri daha verimli ve seçici yapar. Heterojen katalizörlerin bulunduğu ortamlarda ise, tepkimeye giren moleküller katalizör yüzeyinde adsorplanır ve tepkime yüzeyde gerçekleşir. Bu durumun sonucu olarak, heterojen katalizörlerde verim homojen katalizörlere göre daha düşüktür. Ancak, bu homojen katalizörlerin reaksiyon ortamından ayrılması oldukça zordur. Çöktürme ya da distilasyon gibi prosedürlerin uygulanmasını gerektirir. Bilindiği üzere bu işlemler hem zor hem de verim düşüren işlemlerdir. Bazı durumlarda katalizörün tekrar kullanılamaz hale gelmesine bile sebep olabilirler. Bu sebeple, heterojen katalizör dizaynı önemli bir konu haline gelmiştir.

Bu tip birleşme reaksiyonlarında genel olarak literatürde homojen katalizörlerin kullanıldığı görülmektedir. Homojen katalizörlerin bir çok avantajı olmasına rağmen, katalizörü reaksiyon ortamından ayırmak ve tekrar kullanımnı sağlamak çok zordur. Aynı zamanda homojen katalizörleri reaksiyon ortamından ayırmak zor olduğu için bu

tip katalizörler oluşan ürünün saflığını da etkileyebilmektedir. Heterojen katalizörler ise bu bağlamda reaksiyon ortamından kolay ayrılma ve tekrar kullanılabilirlik ve reaksiyon sonunda oluşan atık azaltımı açısından öne çıkmaktadırlar.

Bu tez çalışmasında, ön fonksiyonlandırma olmadan tiol-alkin birleşme reaksiyonlarını sağlamak için, gözenekli bir polimere tutturulan bakır iyonlarının, oksidatif karşılıklı dehidrojenatif çiftleşme reaksiyonu koşulları altında, katalizör olarak çalışıp çalışmadığı incelenmiştir.

Metal katalizörlü oksidatif karşılıklı dehidrojenatif çiftleşme reaksiyonları C-H ve X-H (X=heteroatom) bağlarının direk aktivasyonuna sebep olarak yeni C-C ve/veya C-X bağları oluşumunu sağlamaktadır.

Alkinlerin kendi kendilerine çiftleşme reaksiyonları sebebiyle, sp C-H bağlarının heteroatomlar ile bağ yapmasını sağlamak için aktive edilmesi problem yaratmaktadır. Bu nedenle,direk oxidatif karşılıklı dehdirojenatif birleşme reaksiyonları daha da önem kazanmaktadır. Son yıllarda, terminal alkinlerin nitrojen nükleofilleri ve fosfonatlar ile, hava veya saf O_2 oksidant olarak kullanılarak, direk oxidatif karşılıklı dehdirojenatif birleşme reaksiyonu sonucu C-N ve C-P asetilenlerinin oluşturduğu literatürde belirtilmiştir.

Zhao ve grubu tarafından yapılan yeni bir çalışmada, hekzagonal mezopor bir (MCM-41) malzeme üzerine nitrojen-bakır kompleksi bağlanmış [MCM-41-2N-CuCl] ve bu malzeme yüksek verimli ve tekrar kullanılabilir bir katalizör olarak terminal alkinlerin tioller ile direk oksidatif karşılıklı dehidrojenative birleşme reaksiyonlarında kullanılmıştır. Bu reaksiyonlarda oksidant olarak O_2 kullanılmış ve alkinil sülfitler elde edilmiştir. Mezopor MCM-41 malzemesinin yüksek yüzey alanı genişliği, büyük ve düzenli por büyüklüğü vurgulanmış, bu malzeme üzerine tutturulan bidentat nitrojen-bakır kompleksinin alkin ve tiol arasındaki reaksiyonu katalizlediği raporlanmıştır.

Bu durumda, metal iyonlarının üzerine tutturulacağı gözenekli yüzeyin dizaynı önem kazanmaktadır. Gözenek boyutları ne kadar küçültülürse, yüzey alanının o kadar artacağı bilinmektedir. Ancak, reaksiyonların bu gözeneklerde gerçekleşeceği düşünülürse, gözenek boyutunun da önemli bir parametre olduğu göz önünde bulundurulmalıdır. Eğer ki bir gözenekli polimerde por çapı 50 nm'den büyük ise, bu tip gözenekler makrogözenekli; 2nm ile 50 nm arasında ise mezogözenekli, 2 nm'den küçük ise mikrogözenekli olarak isimlendirilirler. Diğer gözenekli yapılarla karşılaştırıldığında mikrogözenekli yapılar 6461 m^2 $g^{-}1$ yüzey alanına kadar çıkabilmektedirler. Bu tez çalışmasında, düzenli mikrogözeneklli yapıların sentezine odaklanılmıştır. Mikrogözenekli yapıların bir çok değişik kimyasal sentez yöntemlerinin olması da onları ayrıca çekici kılmaktadır. Öte yandan bir çok sentez yönteminin olması, gözenek boyutlarının ve özelliklerinin de, hedef uygulamaların ihtiyacına göre, oldukça hassas bir şekilde kontrol edilmesini sağlamaktadır. Mikrogözenekli organik polimerler aminler, fenoller, alkoller veya karboksili asitler gibi polar pendant fonksiyonel gruplar içerirler. Çünkü bu gruplar metal ile kolaylıkla koordine olabilirler. Aynı zamanda kararlı bir mikrogözenekli yapı için sert bir iskelet gerekmektedir. Bu sert iskelet aromatik konjuge yapılar veya çapraz bağlanmış aromatik yüksek performaslı polimer yapılar tarafından sağlanmaktadır. Bu sebeple, düzenli ve kararlı bir mikrogözenekli polimer sentezleyebilmek için monomerlerin yapısı ve sentez metodu hayati önem taşımaktadır. Bu şekilde dizayn edilen mikrogözenekli organik polimerler, katalizör, sensör veya pil olarak kullanılmakla

berabar, karbon dioksit fiksasyonu, gaz depolanması ve çeşitli kromatografik ayırımlar gibi amaçlar için de kullanılmaktadır.

Çalışmanın ilk bölümünde, sentezinde düşük maliyetli melamin ve terephthalaldehit kullanılarak gözenekli malzeme Schiff baz kimyası kullanılarak elde edilmiştir. Daha sonra, bu gözenekli malzemeye bakır iyonları koordine edilmiş ve Schiff baz network polimeri elde edilmiştir. Bu reaksiyonda melamin üzerindeki primer aminler karbonil grupları ile tepkimeye girerek imin yani Schiff baz yapısını oluşturmuştur. Daha sonra bu yapıdaki nitrojen atomları üzerine bakır tutturulmuştur. Bu polimere ait yüzey analizleri gerçekleştirilmiş, bu analizler sonucunda bakır iyonunun polimere tutunduğu ispatlanmıştır. Bu yüzey analizlerinde, boş polimerin yüzey alanı N_2 ve CO_2 absorpsiyonu ile hesaplanmıştır. Daha sonra bu boşluklara bakır iyonları koordine edildiğinde, doğal olarak yüzey alanında bir azalma görülmesi beklenmiştir ve yapılan analiz sonuçları bu varsayımı desteklemektedir.

Çalışmanın ikinci bölümünde ise, gözenekli Schiff baz ağ polimeri kullanılarak alkil ve tioller arasında oksidatif karşılıklı dehidrojenatif birleşme reaksiyonları gerçekleşmiştir. Aynı zamanda bu yöntem ile ditioller ve dialkinler arasında polimerizasyon reaksiyonları denenmiştir. Daha sonra elde edilen ürünlerin çeşitli spektral yöntemler ve moleküler ağırlık tayini ile karakterizasyonu gerçekleştirilmiştir.

1. INTRODUCTION

In this part, the purpose of this study and the literature review related to the topic is briefly explained.

1.1 Purpose of Thesis

Alkynes are an important class of organic molecules because of their versatile applications in materials science and organic synthesis as building blocks [1]. Sulfur-containing compounds have also a crucial role in synthetic organic chemistry since sulfur moiety acts as an important auxilary functional group [2]. There has been an effort to combine alkynes with sulfur-containing compounds by using metal-acetylides and sulfuryl halides or disulfides [3]. However, these methods require a prefunctionalization progress of terminal alkyne or sulfur-containing coupling partners. This situation causes large number of side product formations which results in a dramatic decrease in the yields of reactions. Harsh reaction conditions, low chemoselectivity, limited number of substrate compounds are the other problems frequently faced by the researchers while dealing with prefunctionalization process [3]. Hence, the discovery of new method to perform these reactions in high yields and better conditions gains a considerable attention.

In this thesis, in order to perform a thiol-alkyne coupling reaction (Figure 1.1) without any prefunctionalization process, a heteregenous copper-catalyzed direct oxidative cross-dehydrogenative coupling of terminal alkynes was studied. Design of a porous network polymer which can form a complex with copper ions should behave as a catalyst for coupling reactions between thiol and alkyne compounds.

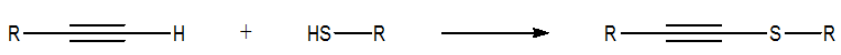


Figure 1.1: Coupling reaction between alkynes and thiols.

1.2 Literature Review

In order to synthesize alkynyl sulfides without prefunctionalization process, researchers have been working on metal-catalyzed oxidative cross-dehydrogenative coupling reaction through the direct activation of C-H and/or X-H bonds (X=heteroatom) for the construction of new C-X bonds [4, 5].

However, due to the risk of homocoupling of terminal alkyne, activation of sp C-H bonds for incorporation with heteroatoms remains as a challenge. Besides, the coupling reactions usually require the use of stoichiometric oxidants such as Cu(I) or Ag(I) salts or organohalides which causes environmental and economic concerns. For these reasons, it is crucial to develop oxidative cross-dehydrogenative coupling reactions. Recently, a few examples of direct oxidative cross-dehydrogenative coupling of terminal alkynes with nitrogen nucleophiles and H-phosphonates using air or O_2 as oxidant to produce C-N and C-P acetylenes have been reported [6].

Despite of these considerable advances, the problem with the homogeneous catalysis still remains to be unsolved. It is difficult to seperate catalyst from reaction mixture and reuse it. In contrast, design of an heteregenous catalysis should take increasingly more attention due to its possible advantages such as reusability, waste minimization derived from reaction workup and help to the development of green chemistry concept. A very new method for the coupling reaction between carbon and heteroatom catalyzed by recyclable copper complexes has been studied by recently [4].

Zhao et al. reported application of a hexagonally-ordered mesoporous material (MCM-41) supported bidentate nitrogen copper(I) complex [MCM-41-2N-CuCl] (Figure 1.2) as a highly efficient and recyclable copper catalyst for the direct oxidative cross-dehydrogenative coupling of terminal alkynes with thiols using O_2 as the sole oxidant under mild conditions to selectively afford a variety of alkynyl sulfides in good to excellent yields [4]. According to their results, mesoporous material (MCM-41) has a extremely high surface area, large and uniform pore size, bidentate nitrogen copper complex can be easily formed and this complex can catalyze the coupling reaction between an alkyne and a thiol [4]. The mechanism proposed for this reaction was shown in Figure 1.3.

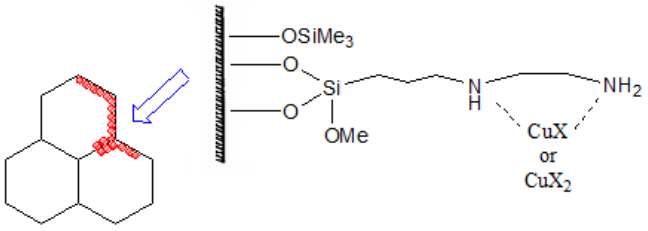


Figure 1.2: MCM-41-2N-CuX(CuX_2) complexes [4].

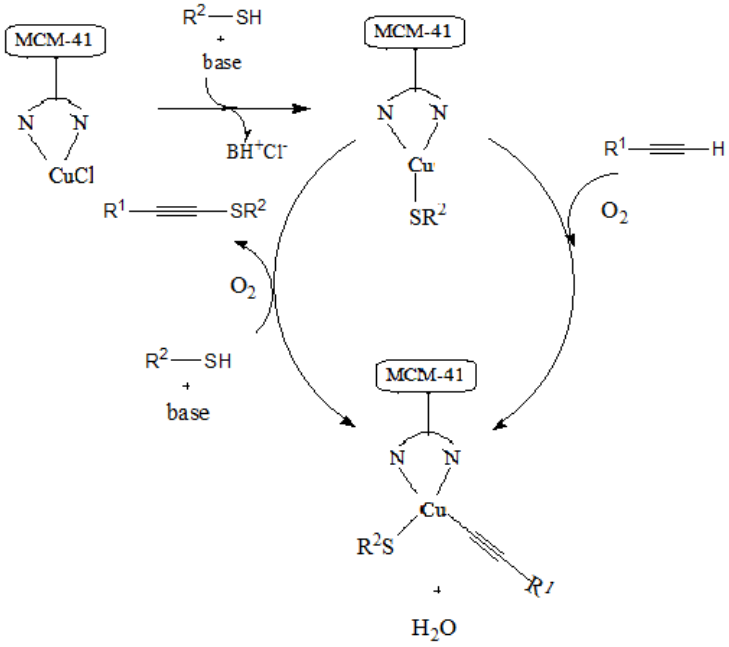


Figure 1.3: Mechanism for heterogeneous copper-catalyzed aerobic cross-dehydrogenative coupling of terminal alkyne with thiol [4].

2. THEORETICAL PART

In this part, the chemistry related to this study was explained in terms of Schiff base chemistry, the characteristics of porous materials and some important coupling reactions in organic chemistry.

2.1 Schiff Base Chemistry

Schiff bases are condensation products of primary amines and carbonyl compounds. These compounds were discovered by a German chemist, Nobel Prize winner, Hugo Schiff in 1864 [7]. A Schiff base (also known as imine or azomethine) is a nitrogen analog of an aldehyde or ketone in which the C=O group is replaced by C=N-R group [8]. The general reaction for Schiff base formation is given in Figure 2.1.

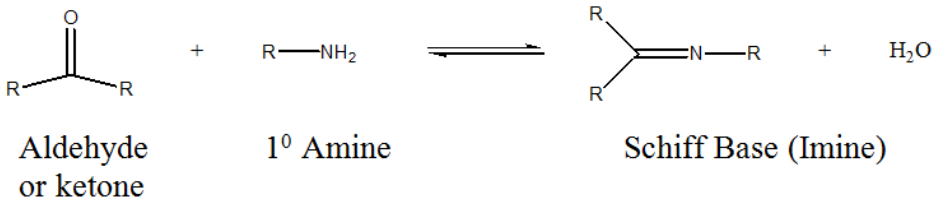


Figure 2.1: Schematic illustration of condensation of an aldehyde or ketone with a primary amine.

Schiff base ligands are essential in the field of coordination chemistry, especially in the development of complexes of Schiff bases. Because these compounds are potentially capable of forming stable complexes with metal ions. Due to the excellent selectivity, sensitivity and stability of Schiff bases for specific metal ions such as Ag(II), Al(III), Co(II), Cu(II), Gd(III), Hg(II), Ni(II), Pb(II), Y(III) and Zn(II), a large number of different Schiff base ligands have been used as cation carriers in potentiometric sensors [9]. Schiff bases and their metal complexes are increasingly being used as catalysts in various biological systems, polymers and dyes [10].

2.1.1 Mechanistic details of Schiff base chemistry

As can be seen in the schematic illustration of Schiff Base chemistry in Figure 2.2, R groups may be an alkyl or aryl group. Schiff bases that contain aryl substituents are substantially more stable and more readily synthesized, while those, which contain alkyl substituents, are relatively unstable. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable while those of aromatic aldehydes having effective conjugation are more stable. The formation of a Schiff base from an aldehydes or ketones is a reversible reaction and generally takes place under acid or base catalysis, or upon heating [11, 12].

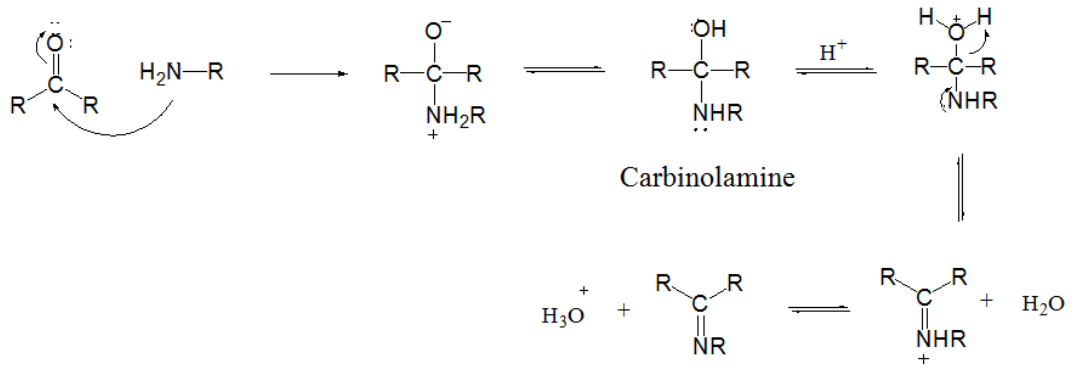


Figure 2.2: Mechanism of Schiff base formation.

In the first part of the mechanism, the amine reacts with the aldehyde or ketone to give an unstable addition compound called carbinolamine. The carbinolamine loses water by either acid or base catalyzed pathways.

Typically, the dehydration of the carbinolamine is the rate-determining step of Schiff base formation and that is why the reaction is catalyzed by acids. Yet, the acid concentration cannot be too high because amines are basic compounds. If the amine is protonated and non-nucleophilic, equilibrium is shifted to the left and carbinolamine formation cannot occur. Therefore, many Schiff bases are best synthesized at mildly acidic pH. The formation is generally driven to the completion by separation of the product or removal of water, or both [8].

Many Schiff bases can be hydrolyzed back to their aldehydes or ketones and amines by aqueous acid or base. In the Figure 2.3, the hydrolysis of a Schiff base is shown.

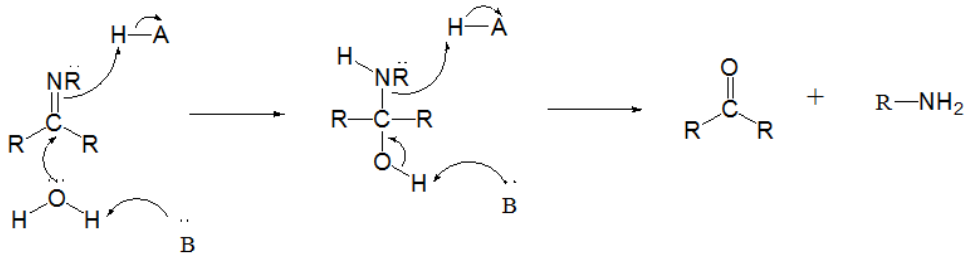


Figure 2.3: Hydrolization of Schiff bases.

2.1.2 Importance and applications of Schiff bases

Nowadays, the research field dealing with Schiff base coordination chemistry has expanded enormously. The importance of Schiff base complexes for bioinorganic chemistry, biomedical applications, supramolecular chemistry, catalysis and material science, separation and encapsulation processes, and formation of compounds with unusual properties and structures have been well recognized and reviewed [13].

Several studies [13–16] showed that the presence of lone pair of electrons on an sp^2 hybridized orbital of nitrogen atom of the azomethine group is of considerable chemical and biological importance. Because of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group, Schiff bases are generally excellent chelating agents [17, 18].

Schiff bases have been reported in terms of their biological properties; such as, antibacterial, antifungal activities [19, 20]. Their metal complexes have been widely studied because they have anticancer and herbicidal applications [21, 22]. They serve as models for biologically important species. *o*-Phenylenediamine Schiff bases show clinical properties [23]. Isatin Schiff bases were reported to possess antiviral, anti-HIV, antiprotozoal and anthelmintic activities [24]. They also exhibit significant anticonvulsant activity, apart from other pharmacological properties [25]. Certain cobalt Schiff base complexes are potent antiviral agents [26]. Schiff bases derived from 4-dimethylamin benzaldehyde shows antibacterial activity. Moreover, these molecules were used as antibodies and anti-inflammatory agents in medicine [27–29].

Schiff base ligands have significant importance in chemistry, especially in the development of Schiff base complexes, because Schiff base complexes are potentially capable of forming stable complexes with metal ions as illustrated in Figure 2.4. Many Schiff base complexes show excellent catalytic activity in various reaction at high

temperature and in the presence of moisture. Over the past few years, there have been many report on their applications as homogeneous and heterogeneous catalysis [30].

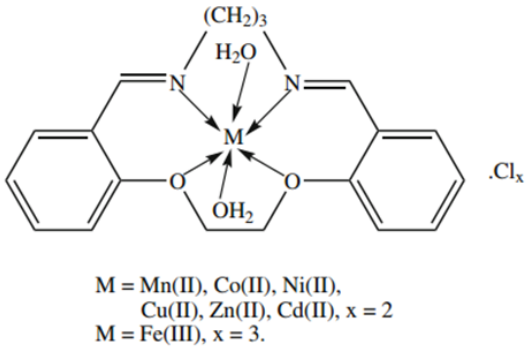


Figure 2.4: An example of Schiff base-metal complex [31].

2.2 Porous Materials

One of the most important studies among researchers is to design and synthesize functional materials. A "functional material" can be defined as a material which behaves in a target-oriented manner. In other words, all properities of a such material are adjusted to serve a specific purpose. Both physical and chemical properities of a material effects the way it behaves in chemical reactions. Acidity or basicity, ability to coordinate to metals, reactivity towards a specific chemical are chemical properities, while electrical and optical specialities, assembling into a certain structure or morphology can be counted as physical properities. The introduction of porosity into a material so as to maximize its accessible surface area is another way to develop its function.

2.2.1 Porosity

Many solid and powder materials both natural (stones, soils, minerals, etc.) and manufactured (catalysts, cement, pharmaceuticals, metal oxides, ceramics, carbons, zeolites, etc.) contain a certain void volume of empty space. This is distributed within the solid mass in the form of pores, cavities, and cracks of various shapes and sizes. The total sum of the void volume is called the porosity [32].

Indeed, useful properties can arise when small pores and thus high surface areas are introduced into a material, which can lead to a number of applications [33]. Porous materials are, for example, used as catalysts or catalyst supports, [34–36] for the

sorption, purification, and storage of gases, [37,38] for electrodes, [39,40] as insulating materials for the semiconductor industry and for optical applications [41].

2.2.2 Properities of porous materials

Porous polymer particles, especially the ones that are spherical in shape, have been utilized in numerous applications for decades. They have been classified as macro-, meso- and microporous depending on the size of the pores, respectively >50 nm, 50–2 nm and <2 nm as illustrated in Figure 2.5 [42].

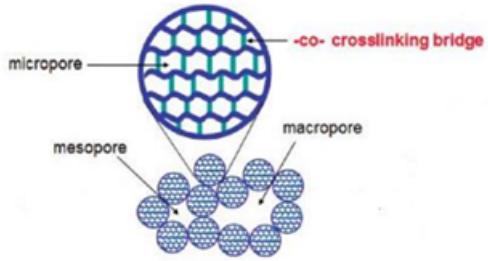


Figure 2.5: Schematic illustration of the size of the pores [43].

Macroporous polymers are characterized by their rigid porous matrix that persists in both the swollen and dry states. The techniques for their preparation were developed in the second half of the 1950's [44]. These polymers have been produced almost exclusively as spherical beads by a suspension polymerization process and used for the preparation of ion exchange resins, chromatographic separation media, catalysts, adsorbents, etc. The macroporous structure results from the phase separation that occurs during polymerization when the polymerization mixture contains both cross-linking and porogenic. Unfortunately, there are no exact rules for the selection of polymerization conditions, and optimization experiments must be carried out for each monomer system selected. Typically, porous properties are controlled by the type of porogen selected and the amounts of both porogen and cross-linker used [45].

Under optimal conditions, the ordered mesoporous polymeric materials exhibited a very narrow pore size distribution (2-50 nm) and a high specific surface area (619 $m^2\ g^{-1}$). The pore size for the meso-/macropores depends on the size of particulate network units themselves and their compact/loose cross-linked aggregation. Attention should be paid to two crucial points with regards to the design and fabrication of meso-/macroporous polymers: (1) exploring an appropriate reaction system, including

reagent, solvent, catalyst and initiator, to guarantee the occurrence of phase separation; and (2) ensuring the appropriate rigidity of the monomer unit and resultant network structure to avoid the collapse of internetwork pores during drying, especially in the case of mesoporous networks [46–48].

When compared with the other porous polymers, microporous polymers are unique in that they exhibit permanent porosity with extremely high BET surface area up to 6461 m^2 g^{-1} [49]. On the other hand, compared with other microporous materials such as zeolites, silicas, and carbons prepared for molecular sieving applications, microporous polymers have an advantage in that they could be prepared via diversified chemical synthetic routes. This provides a wealth of opportunities to control the porous structures as well as framework and surface functionalities to fill to the needs of targeted applications [50]. However, most of these synthetic approaches require costly reaction conditions and use of metal catalysts, which inevitably results in the entrainment of trace amounts of metals in the porous polymers. This results in increased research efforts directed at metal-free synthesis strategies with facile polymerization conditions and low-cost monomers. Some catalyst-free reactions with inexpensive monomers, such as Bakelite type chemistry, Schiff base chemistry and imidization reaction have been developed to prepare microporous network polymers. A typical example is the catalyst-free one-pot preparation of melamine based microporous networks, which was developed via Schiff base chemistry with a large industrial-scale monomer, melamine, and monomers containing multiple aldehyde functional groups. Polymers with high surface area, up to 1500 m^2 g^{-1}, can be obtained with tailorable microporosity by designing the structure of the multialdehyde monomers. The porous framework can possess up to 40 wt % nitrogen, which is very significant for many applications [51, 52].

2.3 Coupling Reactions in Organic Chemistry

A coupling reaction in organic chemistry is a term for reactions in which two fragments are coupled with the help of a special catalyst. As a very broad classification, coupling reactions can be divided into two categories as homocoupling and cross-coupling reactions. When two identical partners are coupled, it is called as homocoupling. The conversion of iodobenzene to biphenyl under required conditions is an example

for that (Figure 2.6). When reaction between two different compounds results in a new bond formation, it is called as cross-coupling reactions. The reaction between bromobenzene and vinyl chloride yielding styrene is an example for cross-coupling reactions (Figure 2.7).

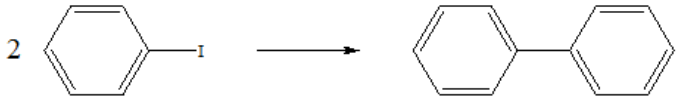


Figure 2.6: An example for homocoupling.

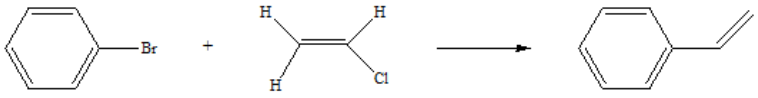


Figure 2.7: An example for cross-coupling.

The cross-coupling of organometallic reagents with organic electrophiles in the presence of group 8-11 metal catalysts, notably nickel, palladium and copper, is the method of choice for a wide range of C-C, C-H, C-N, C-O, C-S, C-P or C-M bond forming processes [53].

2.3.1 Some important transition-metal catalyzed coupling reactions resulted in C-C bond formation

The development of metal-catalyzed cross-coupling reactions over the past 30 years has revolutionized the way, carbon-carbon bonds between sp and sp^2 carbon atoms are formed. These methods have profoundly changed the protocols for the construction of natural products, building blocks for supramolecular chemistry and self-assembly, organic materials and polymers, and lead compounds in medicinal chemistry from simpler entities. The 2010 Nobel prize in chemistry for E. Negishi, R. Heck, and A. Suzuki underlines the importance of direct bond formation betweeen carbon atoms. In this part of thesis, some important carbon-carbon bond forming coupling reactions will be explained.

2.3.1.1 Ullmann reaction

The traditional Ullmann reaction is the homocoupling of aromatic halides mediated by copper at elevated temperatures (Figure 2.8). It was reported by Fritz Ullmann in 1901. Actually, the Ullmann reaction can be taken to refer two different transformations. The first is the copper mediated coupling of two aryl groups to give a biaryl compound; this is the "classic" Ullmann reaction [54]. The second, the Ullmann-type reaction, is the nucleophilic aromatic substitution between aryl nucleophiles and aryl halide, the most common of which is the Ullmann ether synthesis which will be explained in the next subsection of the thesis.

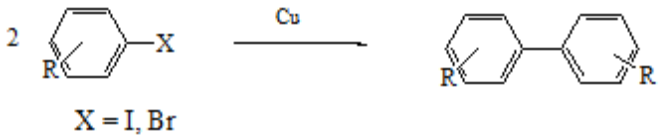


Figure 2.8: Ullmann reaction.

The reaction employing copper was utilized almost exclusively in the following decades for biaryl formation until the rising popularitiy of nickel in Ullmann-type coupling. This was followed by the use of zinc, tin, boron and eventually palladium which is the most commonly used transition metal in organic synthesis today for such transormations [54].

2.3.1.2 Heck reaction

The Heck reaction is the palladium-catalyzed alkenylation or arylation of olefins (Figure 2.9) [55]. It has become one of the most widely used C-C bond forming tools in organic synthesis.

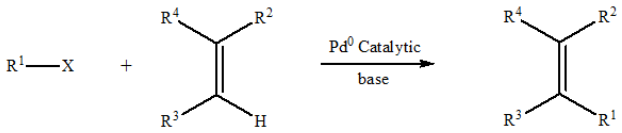


Figure 2.9: General representation of Heck reaction.

Variety of functional groups and substitution patterns on the olefin are tolerated and aryl, alkenyl and some alkyl (lacking β-hydrogen atoms) electrophiles are suitable

reaction partners. The active catalyst is generated *in situ* from a variety of available palladium(0) or palladium(II) precatalysts.

From materials science to enantioselective organic synthesis, nearly every sub-discipline of organic chemistry has embraced the Heck reaction. This reaction may also be considered as a forerunner to all other widely used palladium-catalyzed couplings such as Stille and Suzuki. Perhaps, the greatest social impact of the Heck reaction has been its use in the coupling of alkynes to aryl halides; a reaction which was used to couple fluorescent dyes to DNA bases, allowing the automation of DNA sequencing and the elucidation of human genome [54].

2.3.1.3 Sonogashira reaction

The palladium catalyzed C-C bond formation processes that couples the terminal sp hybridized carbon from an alkyne with and sp^2 carbon of an aryl or vinyl halide to afford a disubstituted alkyne is commonly referred as a Sonogashira coupling (Figure 2.10) [56].

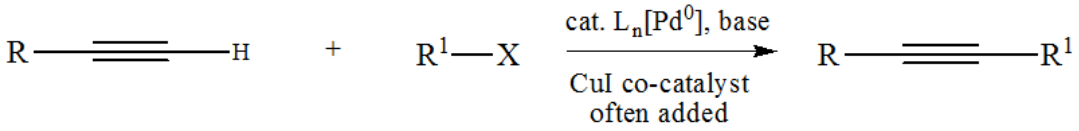


Figure 2.10: General representation of Sonogashira reaction.

The Sonogashira coupling has found a broad utility in complex molecule synthesis. The generic reaction equation does not visually capture the impressive diversity of compounds which have succesfully undergone Sonogashira coupling. This coupling reaction is typically chosen for its mild conditions and corresponding functional group tolerance [54].

2.3.1.4 Stille coupling reaction

The reaction between an organic electrophile and an organostannane mediated by a transition metal catalyst (originally palladium) to form a new sigma carbon carbon bond is referred to as the Stille cross-coupling reaction (Figure 2.11) [54].

The Stille coupling is one of the most powerful tools available to synthetic chemists to date for the formation of sigma carbon carbon bonds. This is demonstrated by the impressive amount of syntheses involving this transformation. One advantage of

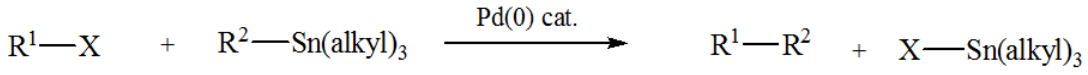


Figure 2.11: General representation of Stille coupling reaction.

this reaction is that it can be performed under very mild and neutral conditions (on the contrary to other cross coupling reactions, like the Suzuki coupling, which are carried out under basic conditions). Furthermore, the organostannane precursors are usually easily accesible, easily purified and stored under normal conditions. There are countless examples reported in the literature over the past 30 years [54].

2.3.1.5 Suzuki reaction

The Suzuki reaction (also referred to as the Suzuki-Miyaura reaction) is the palladium-catalyzed cross coupling of an alkenyl-, aryl- or heteroaryl halide or pseudohalide (R-X) with an alkyl, alkenyl, aryl, or heteroaryl boron reagent (R'-BY_2). This transformation leads to formation of a carbon carbon bond with stereospecific and regiospecific replacement of X with R' (Figure 2.12) [54].

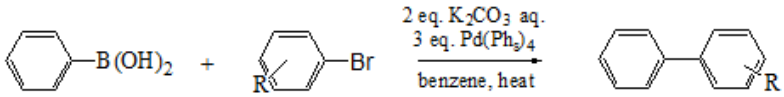


Figure 2.12: Suzuki reaction.

The Suzuki reaction has many advantages; (i) A large number of organoboron coupling partners are commercially available. (ii) The preparation of organoboron compounds can also be accomplished through several different methods. (iii) The organoboron reagents are relatively non-toxic. Moreover, the boron-containing byproducts of the reaction can easily be seperated from the desired product by extarction with aqueous base, which is a problem in Stille reaction.

Although this reaction has many advantages over some other cross coupling reactions, there are three principal limitations in this method. The Suzuki reaction requires the use of either an inorganic base or flouride, which can cause problems for some functionalized substrates. The second limitation is that the organoboron reagents can be difficult to purify. Finally, in contrast to organostannanes, which are relatively nonpolar, organoboron reagents are fairly polar and react with many commonly used

reagents (e.g. oxidants, nucleophiles, bases). With the advantages and disadvantages, this reaction has a lot of variations in the literature [54].

2.3.2 Some important transition-metal catalyzed coupling reactions resulted in C-heteroatom bond formation

Although carbon-carbon bonds comprise the backbone of many organic structures, the function of these organic molecules is often derived from the presence of "heteroatoms", such as nitrogen, oxygen, and sulfur held in these molecules by "carbon-heteroatom bonds." For example, pharmaceuticals and conductive polymers often contain amine C-N bonds, and almost all natural products contain ether, ketone, or ester C-O bonds. Heterocyclic compounds in which C-N or C-O bonds reside in the ring structure are found in all applications of chemistry. Some prominent biologically active molecules – such as the multibillion-dollar drug Nexium (Figure 2.13) – also contain carbon-sulfur bonds. Moreover, useful synthetic intermediates often contain carbon-boron or carbon-silicon bonds that are later converted into carbon-carbon, carbon-oxygen or carbon-nitrogen bonds in the final products [57]. In this part, some important carbon-heteroatom bond forming coupling reactions will be explained.

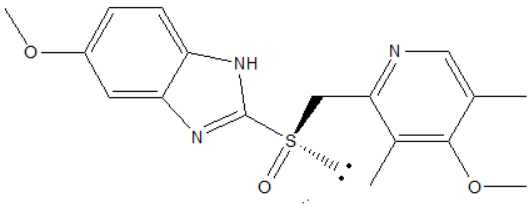


Figure 2.13: Skelatal formula of esomeprazole, original brand name Nexium - a proton pump inhibitor

2.3.2.1 Ullmann condensation

The Ullmann condensation or Ullmann ether synthesis is a variation of the Ullmann reaction, in which a phenol is coupled to an aryl halide to create a diaryl ether in the presence of a copper compound, named after Fritz Ullmann (Figure 2.14). The corresponding aniline or aryl amide reaction is sometimes called Goldberg reaction, named after Irma Goldberg (Figure 2.15) [58].

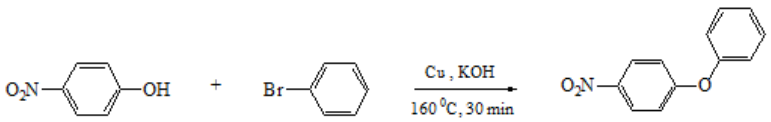


Figure 2.14: Ullmann condensation reaction.

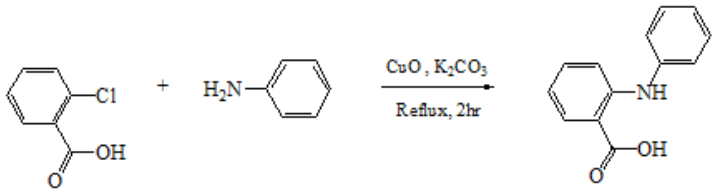
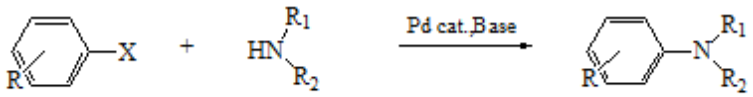


Figure 2.15: Goldberg reaction.

2.3.2.2 Buchwald-Hartwig reaction

The Buchwald–Hartwig amination is a chemical reaction used in organic chemistry for the synthesis of carbon–nitrogen bonds via the palladium-catalyzed cross-coupling of amines with aryl halides (Figure 2.16). The development of the Buchwald–Hartwig reaction allowed for the facile synthesis of aryl amines, replacing to an extent harsher methods (the Goldberg reaction, nucleophilic aromatic substitution, etc.) while significantly expanding the scope of possible C–N bond formation [59].



X = Cl, Br, I, OTf
R_1 = alkyl, aryl, H
R_2 = Alkyl, aryl

Figure 2.16: Buchwald-Hartwig reaction.

Over the course of its development, several generations of catalyst systems have been developed, with each system allowing greater scope in terms of coupling partners and milder conditions, allowing virtually any amine to be coupled with a wide variety of aryl coupling partners. Because of the importance of aryl C-N bonds in pharmaceuticals and natural products, the reaction has gained wide use in synthetic organic chemistry, finding application in many total syntheses and the industrial preparation of numerous pharmaceuticals [60].

2.3.2.3 Chan-Lam coupling

The discovery of efficient palladium-catalyzed amination reactions by Buchwald and Hartwig has been a major breakthrough in the field of carbon-heteroatom couplings, opening up access to a large number of aromatic amines that could only previously be obtained with difficulty using mild and tunable reaction conditions (Figure 2.17). Despite these significant improvements, limitations such as air and moisture sensitivity, functional-group tolerance, and high cost of palladium still exist. Thus, it was reconsidered to use other metal catalysts and results turned back to Ullmann and Goldberg procedures [61]. The Chan–Lam coupling is catalyzed in the presence of copper(II) species and may be conducted in air at room temperature.

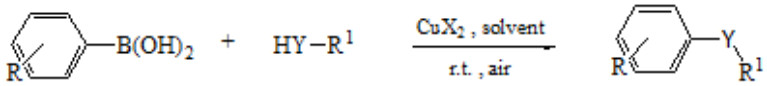


Figure 2.17: Chan-Lam coupling.

The Chan-Lam coupling reaction allows aryl carbon-heteroatom bond formation via the oxidative coupling of aryl boronic acids, stannanes, and siloxanes with N-H or O-H containing compounds in air. Substrates include phenols, amines, anilines, amides, imides, ureas, carbamates, and sulfonamides. The reaction is induced by a stoichiometric amount of copper(II) or a catalytic amount of lower oxidation state copper catalyst reoxidized through atmospheric oxygen. Results indicated that the reaction is broadly applicable to a large variety of substrates and is very tolerant to several sensitive functional groups. [61].

2.3.3 Cross-dehydrogenative coupling (CDC)

The development of methods for forming C-C bonds plays a central role in synthesis design. Historically, nucleophilic additions, substitutions, and Friedel-Crafts-type reactions are the central methods of connecting two simpler molecules to generate a more complex one via the formation of a C-C bond in acyclic structures. The development of pericyclic reactions and transition metal catalyzed reactions increased the efficiency of C-C bond formations in modern organic chemistry and greatly extended their scope. However, since state-of-the-art C-C bond formation reactions

must use prefunctionalized starting materials, transition metal catalyzed C-H bond activation and subsequent C-C bond formations have attracted much interest in recent years. Scientists have been exploring the possibility of constructing functional molecules by only using C-H bonds under oxidative conditions (via in situ generation of various reactive intermediates), a method that is termed as cross-dehydrogenative coupling (Figure 2.18) [62]. A comparison between a classical cross coupling and cross dehydrogenative coupling was shown in Figure 2.19

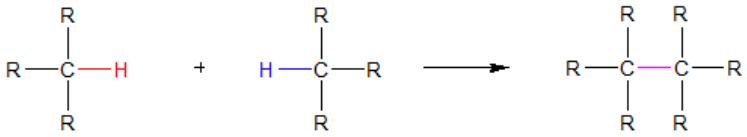


Figure 2.18: Cross-dehydrogenative coupling.

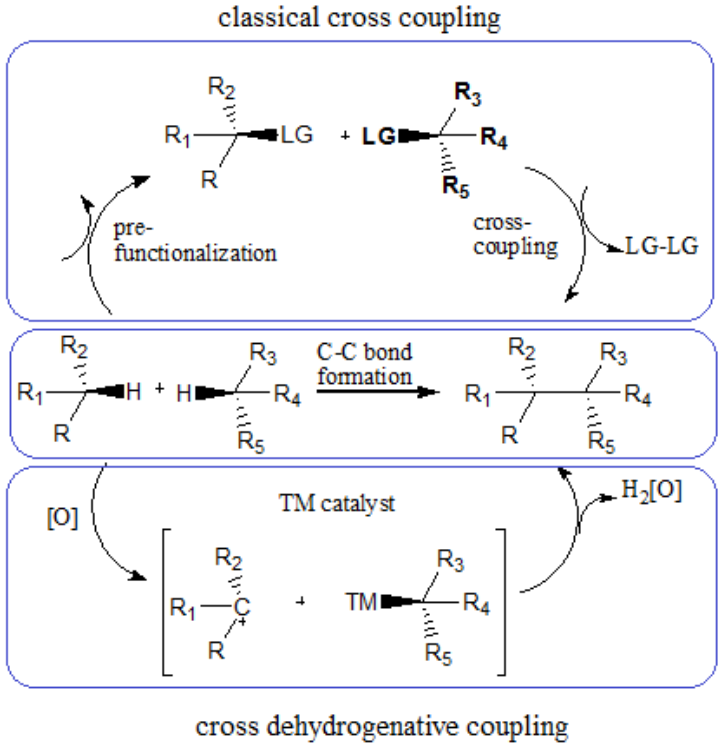


Figure 2.19: Differences between classic cross coupling and cross-dehydrogenative coupling [63].

The idea behind the cross-dehydrogenative coupling was to use unconventional chemical reactivities which could simplify synthesis, decrease overall waste and maximize resource utilization. As recent studies show, the goals are almost achieved.

Some successful examples from the recent literature are given in Figure 2.20 and Figure 2.21:

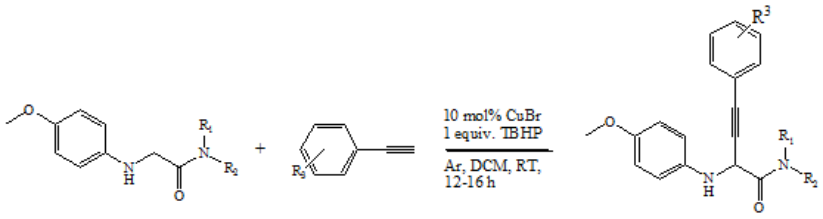


Figure 2.20: Direct alkynylation of Glycine amides via CDC reaction [62].

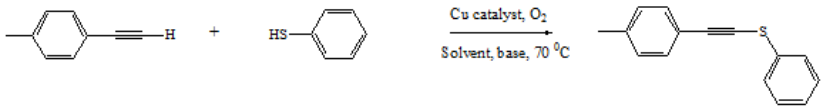


Figure 2.21: CDC Reaction of 4-methylphenylacetylene with thiophenol [4].

3. EXPERIMENTAL

In this part of thesis, the detailed information regarding the chemicals used and synthesis and characterization methods were explained.

3.1 Materials and Chemicals

3.1.1 Chemicals

Melamine (99%, Sigma-Aldrich) was used as received.

Terephthalaldehyde (99%, Sigma-Aldrich) was used as received.

Copper (I) bromide (CuBr, $\geq$98.0%, Sigma-Aldrich) was used as received.

Thiophenol ($\geq$99.0%, Sigma-Aldrich) was used as received.

Phenylacetylene ($\geq$98.0%, Sigma-Aldrich) was used as received.

Propargyl alcohol (99%, Sigma-Aldrich) was used as received.

Propargyl bromide solution (80 wt. % in toluene, contains 0.3% magnesium oxide as stabilizer, Fluka) was used as received.

1-Butanethiol (99%, Sigma-Aldrich) was used as received.

1,6-hexanedithiol (96%, Fluka) was used as received.

1,2-ethanedithiol ($\geq$98.0%, Sigma-Aldrich) was used as received.

1,3-propandithiol (99%, Sigma-Aldrich) was used as received.

1,4-diethynylbenzene (96%, Sigma-Aldrich) was used as received.

Magnesium Sulfate ($\geq$99.h%, Sigma-Aldrich) was used as received.

Potassium Carbonate ($\geq$99.h%, Sigma-Aldrich) was used as received.

3.1.2 Solvents

N,N-Dimethyl formamide (DMF, 99.0 %, Aldrich) was used as received.

Tetrahydrofuran (THF, 99.8%, J.T.Baker) was used as received.

Methanol (Technical) was used for the precipitation of polymers without further purification.

Chloroform (≥99%, Aldrich) was used as received.

Acetone (99%, Aldrich) was used as received.

Dichloromethane (≥99%, J.T. Baker) was used as received.

Dimethyl sulfoxide (DMSO, ≥99.5%, Sigma) was used as received.

1,4-dioxane (≥99.0%, Sigma-Aldrich) was used as received.

3.2 Characterization

3.2.1 Nuclear magnetic resonance spectroscopy (NMR)

^{1}H NMR spectra of 5–10 % (w/w) solutions in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard were recorded at room temperature at 500 MHz on a Bruker DPX 250 spectrometer.

3.2.2 Infrared spectrophotometer (FT-IR)

FT-IR spectra were recorded on a Perkin Elmer FTIR Spectrum One B spectrometer.

3.2.3 Gel-permeation chromatography

Molecular weights of the polymers soluble in organic solvents were determined by a gel permeation chromatography (GPC) instrument, Viscotek GPCmax Autosampler system, consisting of a pump, three ViscoGEL GPC columns (G2000HHR, G3000HHR, and G4000HHR), and a Viscotek differential refractive index (RI) detector with a THF flow rate of 1.0 mL min^{-1} at 30 ^{o}C. The RI detector was calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. GPC measurements with the water-soluble polymers were performed at room temperature with a setup consisting of a pump (HP 1050), a refractive index detector (HP 1047A), and three highresolution Waters columns (AQ3.0, AQ4.0, and AQ5.0). The effective molecular weight ranges were 1000-60000, 10000-400000, and 50000-4000000, respectively. Water was used as eluent at a flow rate of 0.5 mL/min at room temperature. Data analyses were performed with HP Chemstation Software. Calibration with linear poly (ethylene oxide) standards (Polymer Laboratories) was used to estimate the molecular weights.

3.3 Preparation of Microporous SNW Polymer

A flame-dried Schlenk flask was fitted with a condenser and a magnetic stirring bar was charged with melamine (500 mg, 3.96 mmol), terephthalaldehyde (1000 mg, 7.45 mmol), and DMSO (15.5 mL) (Figure 3.1). After degassing by nitrogen bubbling the mixture was heated to 180 ^{o}C for 72 h under an inert atmosphere. After cooling to room temperature, the precipitated porous network was isolated by filtration over a Buchner funnel and washed with excess acetone, tetrahydrofuran, and chloroform. After washing the precipitated material with DMSO, tetrahydrofuran (THF) methanol, and finally 1,4-dioxane, all samples were freeze-dried using 1,4-dioxane as swelling solvent. The product was collected as rigid yellow powders in 62% yield. No variation was observed in the material properties after exposure of the wholly insoluble powders to humidity and/or acidic or basic conditions.

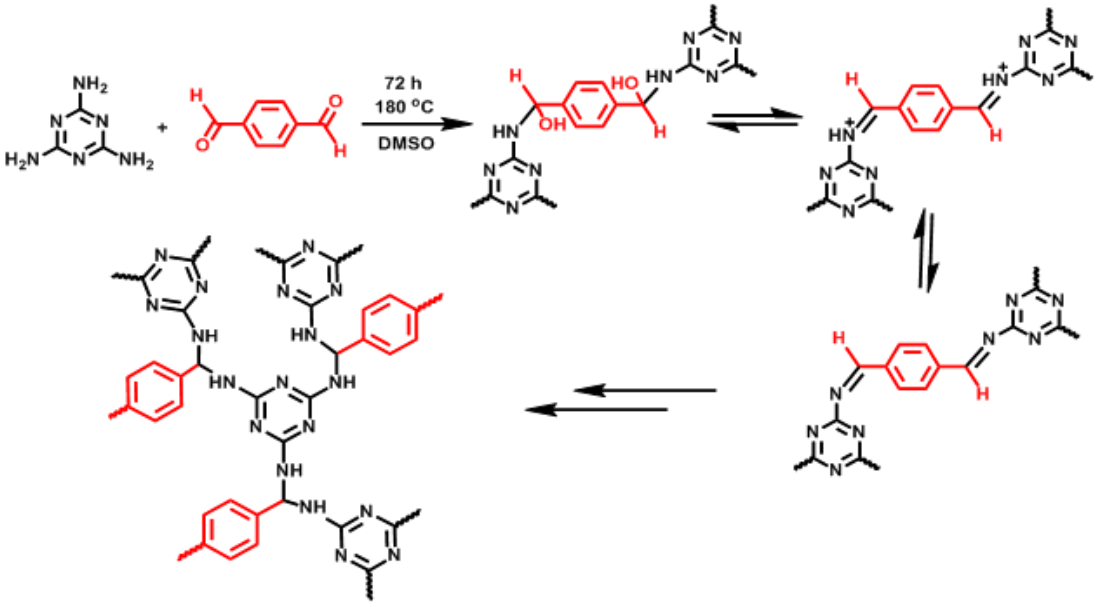


Figure 3.1: General mechanism for the preperation of the microporous SNW polymer.

3.4 Preparation of Copper (I) Incorporated Schiff Base Network (SNW) Polymer

A solution of CuBr (30 mg) in DMF (50 mL) was added to a 250 mL round-bottomed flask charged with the off-yellow SNW powder (500 mg), and the mixture was stirred at room temperature for 72 h to yield the gray-green-colored Cu(I)-loaded microporous polymer (Figure 3.2). The solid particles were filtrated and washed with excess DMF and acetone.

3.5 Preparation of Copper (II) Incorporated Schiff Base Network (SNW) Polymer

A solution of $CuBr_2$ (30 mg) in DMF (50 mL) was added to a 250 mL round-bottomed flask charged with the off-yellow SNW powder (500 mg), and the mixture was stirred at room temperature for 72 h to yield the gray-green-colored Cu(II)-loaded microporous polymer. The solid particles were filtrated and washed with excess DMF and acetone.

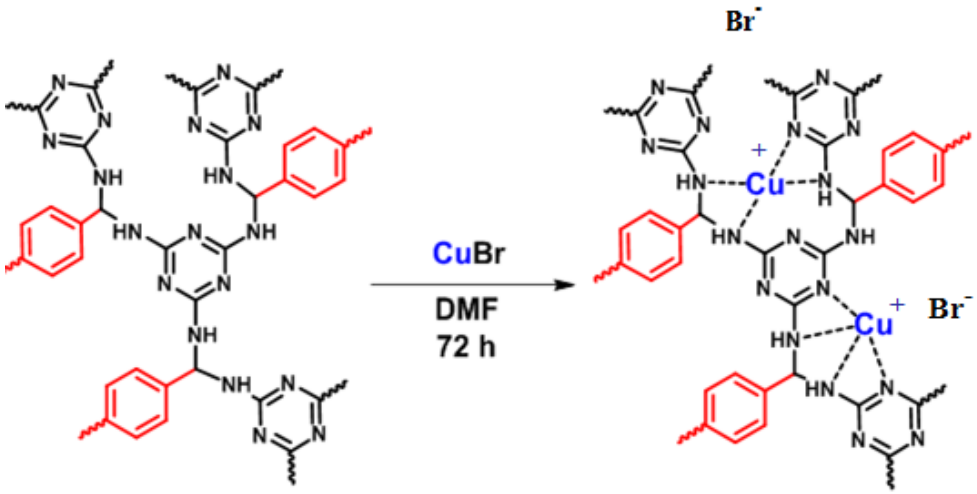


Figure 3.2: Coordination of Copper ions into the SNW polymer.

3.6 General Procedures for Thiol – Alkyne Reactions

In a typical experiment, Pyrex tube was filled with equivalent amounts of thiol and alkyne compound, Cu(I)/SNW, and DMSO and K_2CO_3 (%10 mmol in H_2O). This mixture was stirred at 70 ^oC for 1.5 hour under 1 atm. of O_2. After the reaction, Cu(I)/SNW was filtered and the resultant filtrate was extracted with DCM and water twice. The organic extracts were combined and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The obtained products wew analyzed with NMR Spectroscopy.

Phenyl (phenylethynyl) sulfide without copper (1)

Pyrex tube was filled with thiophenol (1 ml, 9.73 mmol), phenyl acetylene (1.014 ml, 9.73 mmol), and DMSO (2 mL) and K_2CO_3 (0.973 mmol in 2 ml H_2O). This mixture was stirred at 70 ^oC for 1.5 hour under 1 atm. of O_2. After the reaction, mixture was extracted with DCM and water twice. The organic extracts were combined and

dried over $MgSO_4$. The solvent was evaporated under reduced pressure. No product formation was observed.

Phenyl (phenylethynyl) sulfide with CU(I)SNW (2)

Pyrex tube was filled with thiophenol (1 ml, 9.73 mmol) mmol), phenyl acetylene (1.014 ml, 9.73 mmol), Cu(I)/SNW (100 mg), and DMSO (2 mL) and K_2CO_3 (0.973 mmol in 2 ml H_2O). This mixture was stirred at 70 ^oC for 1.5 hour under 1 atm. of O_2. After the reaction, Cu(I)/SNW was filtered and the resultant filtrate was extracted with DCM and water twice. The organic extracts were combined and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The resulting product was obtained as pale yellow oil. The obtaied oil was analyzed with NMR and the following results were obtained (Figure 3.3). ^{1}H NMR (500 MHz $CDCl_3$) : δ 7.27 - 7.53 ppm (m, 10 H).

Phenyl (phenylethynyl) sulfide with CU(II)SNW (3)

Pyrex tube was filled with thiophenol (1 ml, 9.73 mmol), phenyl acetylene (1.014 ml, 9.73 mmol), Cu(II)/SNW (100 mg), and DMSO (2 mL) and K_2CO_3 (0.973 mmol in 2 ml H_2O). This mixture was stirred at 70 ^oC for 1.5 hour under 1 atm. of O_2. After the reaction, Cu(II)/SNW was filtered and the resultant filtrate was extracted with DCM and water twice. The organic extracts were combined and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The resulting product was obtained as pale yellow oil. The obtaied oil was analyzed with NMR and the following results were obtained (Figure 3.3). ^{1}H NMR (500 MHz $CDCl_3$) : δ 7.27 - 7.53 ppm (m, 10 H).

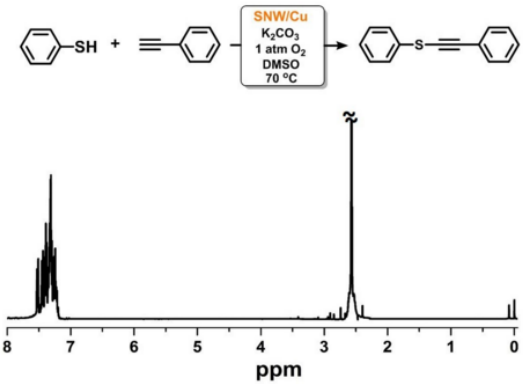


Figure 3.3: ^{1} H NMR of Phenyl (phenylethynyl) sulfide.

Phenyl (1-hydroxypropynyl) sulfide (4)

Pyrex tube was filled with thiophenol (1 ml, 9.73 mmol), propargyl alcohol (0.566 ml, 9.73 mmol), Cu(I)/SNW (100 mg), and DMSO (2 mL) and K_2CO_3 (0.973 mmol in 2 ml H_2O). This mixture was stirred at 70 ^oC for 1.5 hour under 1 atm. of O_2. After the reaction, Cu(I)/SNW was filtered and the resultant filtrate was extracted with DCM and water twice. The organic extracts were combined and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The resulting product was obtained as pale yellow oil. The obtaied oil was analyzed with NMR and the following results were obtained (Figure 3.4). ^{1}H NMR (500 MHz $CDCl_3$) : δ 3.80 ppm (br, 2H), δ 7.55-7.45 ppm (m, 5H).

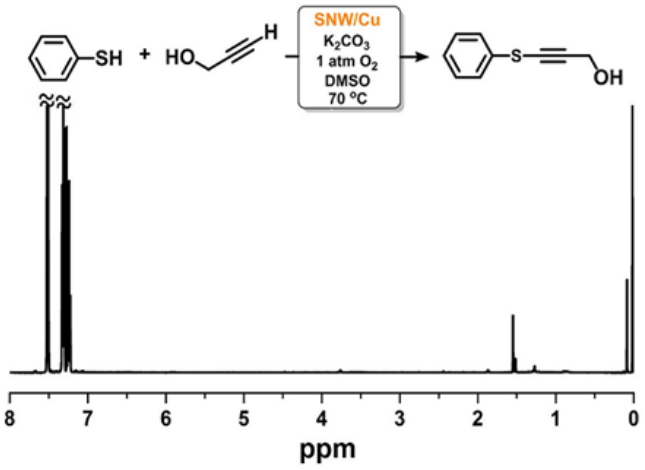


Figure 3.4: ^{1} H NMR of Phenyl (1-hydroxypropynyl) sulfide.

Phenyl (1-bromopropynyl) sulfide (5)

Pyrex tube was filled with thiophenol (1 ml, 9.73 mmol), propargyl bromide (0.867 ml, 9.73 mmol), Cu(I)/SNW (100 mg), and DMSO (2 mL) and K_2CO_3 (0.973 mmol in 2 ml H_2O). This mixture was stirred at 70 ^oC for 1.5 hour under 1 atm. of O_2. After the reaction, Cu(I)/SNW was filtered and the resultant filtrate was extracted with DCM and water twice. The organic extracts were combined and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The resulting product was obtained as pale yellow solid. The obtaied oil was analyzed with NMR and the following results were obtained (Figure 3.5). ^{1}H NMR (500 MHz $CDCl_3$) : δ 2.63 ppm (s, 2H), δ 7.55-7.45 ppm (m, 5H).

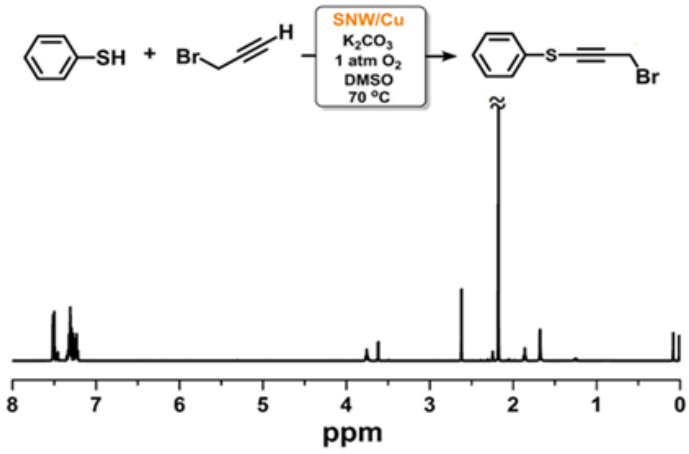


Figure 3.5: [1] H NMR of Phenyl (1-bromopropynyl) sulfide.

Butyl (1-hydroxypropynyl) sulfide (6)

Pyrex tube was filled with butanethiol (1 ml, 9.28 mmol), propargyl alcohol (0.540 ml, 9.28 mmol), Cu(I)/SNW (100 mg), and DMSO (2 mL) and K_2CO_3 (0.928 mmol in 2 ml H_2O). This mixture was stirred at 70 ^oC for 1.5 hour under 1 atm. of O_2. After the reaction, Cu(I)/SNW was filtered and the resultant filtrate was extracted with DCM and water twice. The organic extracts were combined and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The resulting product was obtained as pale yellow solid. The obtaied oil was analyzed with NMR and the following results were obtained (Figure 3.6). ^{1}H NMR (500 MHz $CDCl_3$) : δ 4.57 ppm (s, 2H), δ 3.60 ppm (t, 2H), δ 1.53 ppm (m, 2H), δ 1.3 ppm (m, 2H), δ 0.90 ppm (t, 3H),

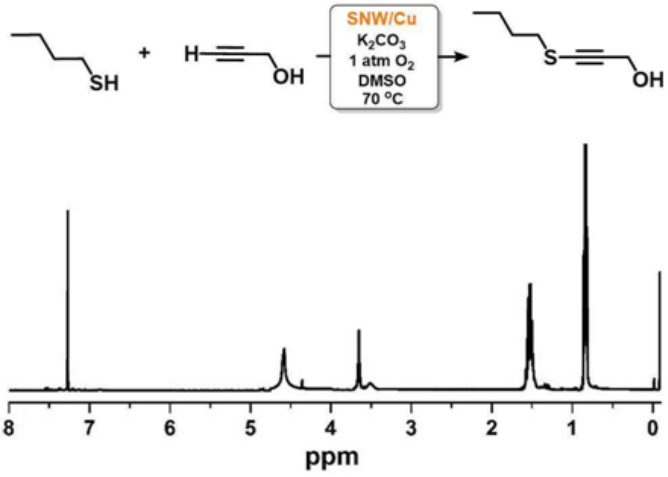


Figure 3.6: [1] H NMR of Butyl (1-hydroxypropynyl) sulfide.

Butyl (phenylethynyl) sulfide (7)

Pyrex tube was filled with butanethiol (1 ml, 9.28 mmol), phenyl acetylene (1.019 ml, 9.28 mmol), Cu(I)/SNW (100 mg), and DMSO (2 mL) and K_2CO_3 (0.928 mmol in 2 ml H_2O). This mixture was stirred at 70 ^oC for 1.5 hour under 1 atm. of O_2. After the reaction, Cu(I)/SNW was filtered and the resultant filtrate was extracted with DCM and water twice. The organic extracts were combined and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The resulting product was obtained as pale yellow oil. The obtaied oil was analyzed with NMR and the following results were obtained (Figure 3.7). ^{1}H NMR (500 MHz $CDCl_3$) : δ 0.95 ppm (t, 3H), δ 1.48 ppm (m, 2H), δ 1.70 ppm (m, 2H), δ 2.80 ppm (t, 2H), δ 7.27-7.41 ppm (m, 5H).

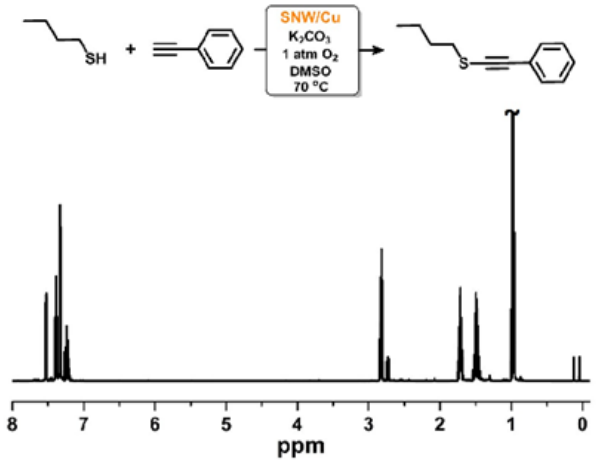


Figure 3.7: ^{1} H NMR of Butyl (phenylethynyl) sulfide.

2-aminoethyl (phenylethynyl) sulfide (8)

Pyrex tube was filled with 2-aminoethanethiol (0.5 g, 6.48 mmol), phenyl acetylene (0.712 ml, 6.48 mmol), Cu(I)/SNW (100 mg), and DMSO (2 mL) and K_2CO_3 (0.648 mmol in 2 ml H_2O). This mixture was stirred at 70 ^oC for 1.5 hour under 1 atm. of O_2. After the reaction, Cu(I)/SNW was filtered and the resultant filtrate was extracted with DCM and water twice. The organic extracts were combined and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The resulting product was obtained as pale yellow oil. The obtaied oil was analyzed with NMR and the following results were obtained (Figure 3.8). ^{1}H NMR (500 MHz $CDCl_3$) : δ 3.01 ppm (t, 2H), δ 4.12 ppm (q, 2H), δ 7.27-7.41 ppm (m, 5H).

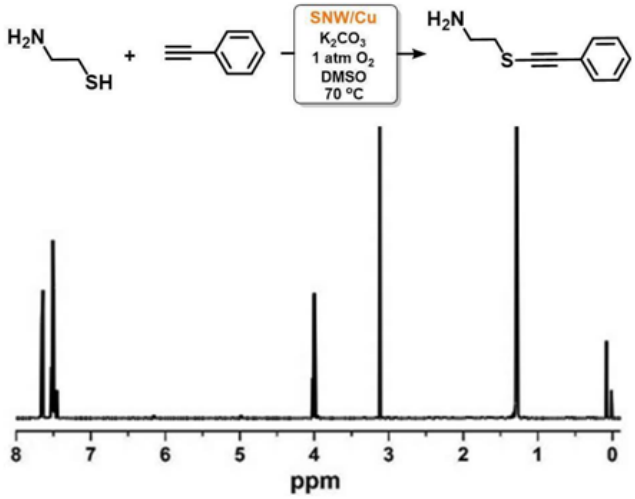


Figure 3.8: [1] H NMR of 2-aminoethyl (phenylethynyl) sulfide.

1,4-bis(butylthio)ethynyl benzene (9)

Pyrex tube was filled with butanethiol (1.0 ml, 9.28 mmol), 1,4-diethynylbenzene (0.585 g, 4.64 mmol), Cu(I)/SNW (100 mg), and DMSO (2 mL) and K_2CO_3 (0.464 mmol in 2 ml H_2O). This mixture was stirred at 70 ^oC for 1.5 hour under 1 atm. of O_2. After the reaction, Cu(I)/SNW was filtered and the resultant filtrate was extracted with DCM and water twice. The organic extracts were combined and dried over $MgSO_4$. The solvent was evaporated under reduced pressure. The resulting product was obtained as pale yellow oil. The obtaied oil was analyzed with NMR and the following results were obtained (Figure 3.9). ^{1}H NMR (500 MHz $CDCl_3$) : δ 0.9 ppm (t, 3H), δ 1.30 ppm (m, 2H), δ 1.52 ppm (m, 2H), δ 3.23 ppm (t, 2H) δ 7.27-7.41 ppm (m, 5H).

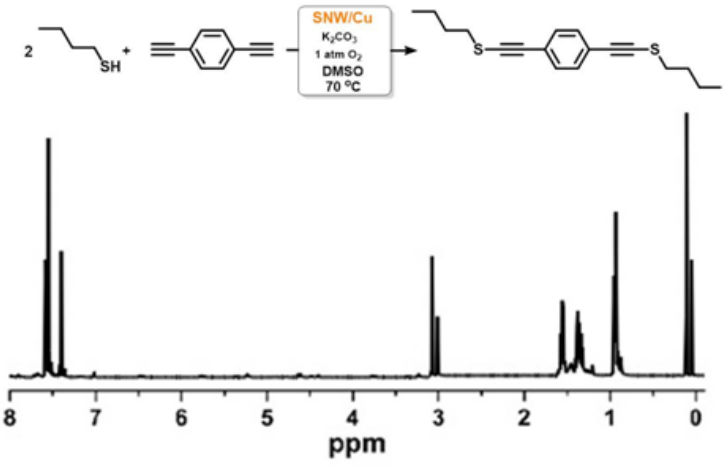
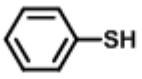
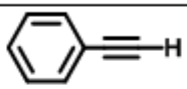
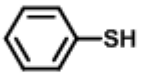
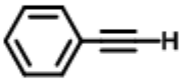
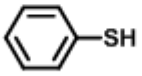
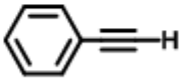
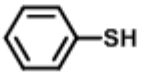
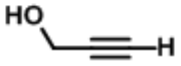
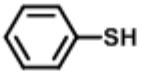
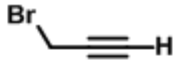
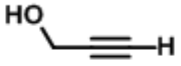
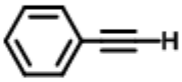
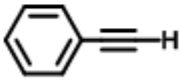
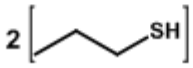
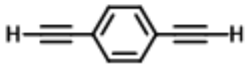


Figure 3.9: [1] H NMR of 1,4-bis(butylthio)ethynyl benzene.

The summary of reactants and yields are given in Table 3.1 :

Table 3.1: The list of synthesized thiol-alkyne compounds.

Entry	Thiol	Alkyne	Catalyst	Yield %
1			No copper	No reaction
2			SNW/Cu(I)	54
3			SNW/Cu(II)	55
4			SNW/Cu(I)	57
5			SNW/Cu(I)	48
6			SNW/Cu(I)	60
7			SNW/Cu(I)	52
8			SNW/Cu(I)	59
9			SNW/Cu(I)	57

3.7 General Procedures for Polymerization Reactions

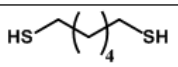
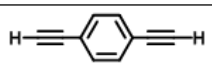
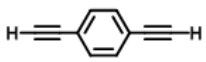
Reactions was performed using a terminal dialkyne (0.5 mmol), dithiol (0.5 mmol), Cs_2CO_3 (0.05 mmol) and copper-incorporated Schiff base network polymer (Cu(I)SNW) (0.025 mmol) in DMSO (2 mL) at 70^{o}C under O_2 atmosphere for 24 hour. Upon completion, the reaction mixture was cooled to room temperature. Cu(I)SNW catalyst and the resulting polymer were filtered off and the solids were dissolved in THF. Since the Cu(I)SNW does not dissolve in THF, it was removed by filtration and the solvent was evaporated in vacuo. At the end, the polymer was precipitated in cold methanol.

1,6-hexanedithiol - 1,4-diethynylbenzene polymer

Pyrex tube was filled with 1,6-hexanedithiol (1 ml, 6.54 mmol), 1,4-diethynylbenzene (0.825 g, 6.54 mmol), Cu(I)/SNW (100 mg), and DMSO (2 mL) and Cs_2CO_3 (0.05 mmol). This mixture was stirred at 70 ^{o}C for 1.5 hour under 1 atm. of O_2. After the reaction, Cu(I)/SNW was filtered and the resultant filtrate was evaporated under reduced pressure. Resulting polymer was precipitated from cold methanol. The obtained polymer was analyzed with GPC.

The results of polymerization studies are shown in Table 3.2 :

Table 3.2: Polymerization studies

[a]Entry	Thiol	Alkyne	Catalyst	Conv. (%)	[b]$M_{n,(GPC)}$ (g mol^{-1})	PDI
1			SNW/Cu(I)	65	3.100	1.31
2			Cu(I)/PMDETA	94	150.000	2.65

[a]Polymerizations were carried out in a Schlenk tube at 70 °C for 24 h. The polymers were precipitated in methanol. [b]Determined by GPC, according to polystyrene standards.

3.8 Leaching Test

The heterogeneity of the Cu(I)/SNW catalyst was examined by the leaching test under the same reaction conditions to detect copper was leaching out from the solid to the solution. The model reaction was carried out for 200 min and then the catalyst was filtered. A fraction from the product phase was measured using Atomic Absorption Spectroscopy (AAS) to determine the amount of copper residue. No copper was detected up to ppb level, only negligible levels of Cu(I) leaching was observed.

4. RESULTS AND DISCUSSION

In this thesis study, the synthesis of a Schiff base network polymer (SNW) by using melamine and terephthalaldehyde and copper ions were incorporated into this polymer. Afterwards, this polymer was used as a heteregenous catalysis for the oxidative cross-dehydrogenative coupling of thiol and alkyne compunds.

Since thiol-alkyne complexes are very important compunds in synthetic organic chemistry; an efficient, cheap and green synthesis methodology may lead to major applications. With the help of designed copper incorporated Schiff base network polymer, as catalyst, the couplings of various thiols and alkynes were succesfully achieved.

4.1 Melamine - Terephthalaldehyde Based Microporous Schiff Base Network Polymer

In our synthetic strategy, the monomers, namely melamine and terephthalaldehyde were heated in dimethyl sulfoxide under inert conditions to form the Schiff base microporous polymer network (SNW). In this process, the primary amines of the melamine react with the carbonyl group forming intermediates imine or Schiff-bases which essentially yield the desired network polymer CP-MASS ^{13}C-NMR spectrum of SNW is displayed as Figure 4.1 : A sharp carbon signal appears at 140 ppm belonging to terephthalaldehyde aromatics. Morever, the aminal carbons exhibit signals between 75 and 80 ppm indicating most of the crosslinking is comprised of aminal linkages.

The structures of SNW and Cu(I)/SNW were confirmed by Fourier transform infrared (FTIR) spectral analysis (Figure 4.2). In the FTIR spectrum, the bands corresponding to the amino group of melamine appear between ca. 3500 and 3200 cm^{-1} (NH stretching) and the bands for the carbonyl function of the aldehyde group at 2857 cm^{-1} (C–H stretching). Also, C=O stretching of the aldehyde function is visible at 1730 cm^{-1}. The presence of distinct bands corresponding to the quadrant and semicircle stretching of the triazine ring at 1543 cm^{-1} and 1474 $^{-1}$, respectively,

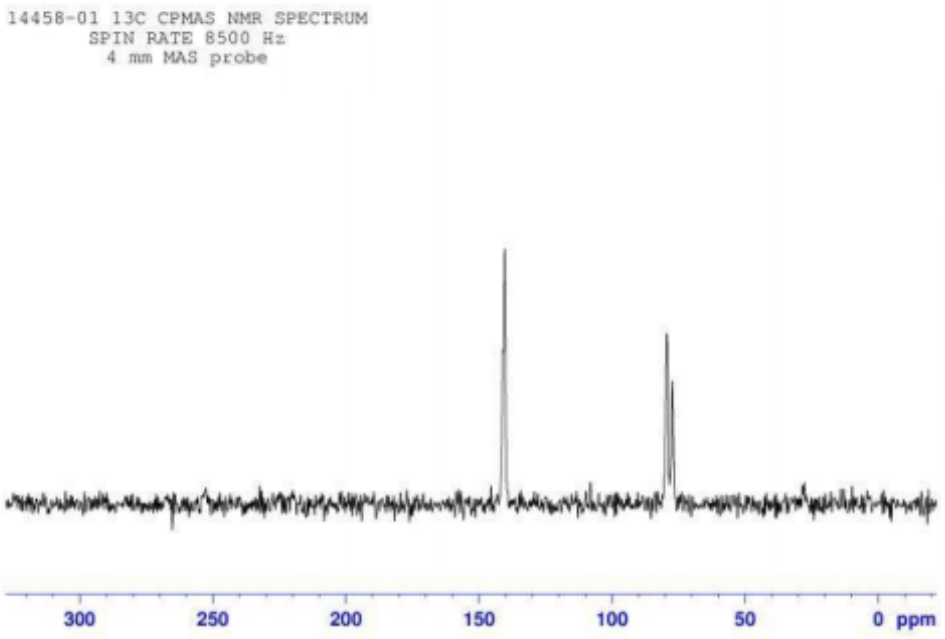


Figure 4.1: CP-MASS ^{13}C-NMR spectrum of SNW.

confirms the successful incorporation of melamine into SNW through aminal linkages. After treatment with CuBr solution, –NH deformation band at 1651 cm^{-1} and the –NH stretching bands became more distinguishable thus evidencing the complex formation.

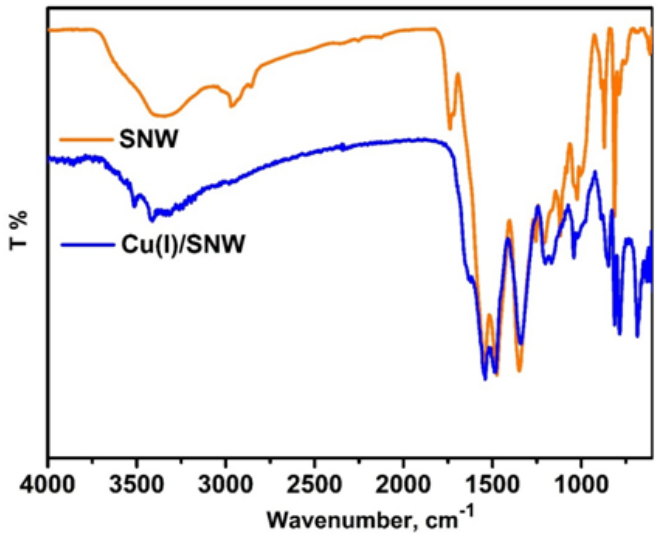


Figure 4.2: FTIR spectra of SNW and Cu(I)/SNW.

The porosity of SNW and Cu(I)/SNW was evidenced by N_2 (at 77.4 K) and CO_2 (at 273.15 K) adsorption/desorption analysis. N_2 analysis showed of SNW showed an isotherm that is commonly observed for MOPs (4.3). There is a clear indication of some microporosity (SBET = 295 m^2g^{-1}), indicated by the high level of N_2 adsorption

at low p/p0 (Figure 4.3). Additionally, it is observed that the isotherm shows a very high uptake of N_2 at high p/p0 without showing a mesopore type hysteresis. Such behavior is commonly observed for nanoparticulate and agglomerated species and it can be expected that the SNW is obtained as small, agglomerated microporous particles. Such small particle size reduces diffusional limitations and provides enhances mass transport, which is probably beneficial for catalytic applications.

The isotherm shape does not change significantly after Cu(I) loading and again a steep increase is observed at high p/p0. The slightly changed pattern (compared to pure SNW) can be explained by slight morphological changes that are due to reswelling/redrying the polymer during the loading protocol. A more significant change is observed in the micropore region (low p/p0), where a much lower uptake is observed, resulting in a lowered BET surface area (SBET = 184 m^2g^{-1}).

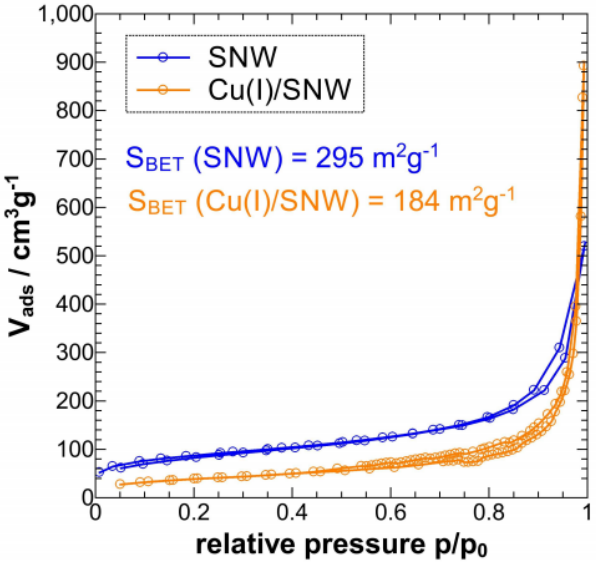


Figure 4.3: N_2 adsorption/desorption analysis of SNW and Cu(I)/SNW at 77.4 K.

It is well known that N_2 analysis at low temperatures can underestimate microporosity and we analyzed the materials also by CO_2 adsorption, which gives additional information on the microporosity of materials. Figure 4.4 shows the CO_2 adsorption/desorption isotherms and again a lower uptake is found for Cu(I)/SNW compared to the parent SNW. Notably, the micropore surface area of SNW is decreased from 548 m^2g^{-1} to 306 m^2g^{-1} after the incorporation of copper species to the network polymer ras determined by GCMC analysis.

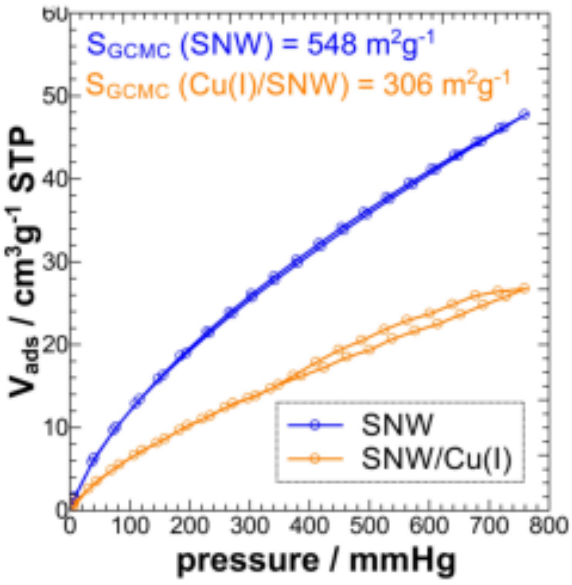


Figure 4.4: CO_2 adsorption/desorption isotherms of the SNW and Cu(I)/SNW.

4.2 Thiol - Alkyne CDC Reactions

In this part, direct oxidative cross-dehydrogenative coupling reactions of various terminal alkynes and thiols by using a copper-incorporated heterogenous catalyst were investigated. The alkyne and thiol substrates are outlined in Table 1. The coupling of phenylacetylene with thiophenol was selected as a model reaction. Disappearance of –SH proton peak at 3.40 ppm and acetylene proton peak at 3.0 ppm in ^{1}H NMR spectrum proved the formation of phenyl (phenylethynyl) sulfide. As shown in Table 1, variety of alkynes could couple with thiols resulting in the formation of the corresponding alkynyl sulfides in good yields. All of them were analyzed by following the disapperance of corresponding –SH and acetylene proton.

Also, polymerization reaction between a dialkyne and dithiol monomers was investigated. The initial procedure was applied, equimolar dialkyne and dithiol monomers in the presence of K2CO3 as a base dissolved in small amount of water and DMSO as reaction solvent for 1.5hour at 700C under O2 atmosphere . But, the polymerization did not occur under this circumstances. GPC analysis showed that only oligomers were formed. When the reaction time increased to 24 hour under same conditions, the molecular weight increased but it was not enough. Then K2CO3 dissolved in small of amount of water was replaced with Cs2CO3 which has a slight solubility in DMSO. The reaction mixture was stirred 24 hour at 700C under

O2 atmosphere and an significant increase in molecular weight of the polymer was observed. But it has been not achieved to increase it further. When the same reaction was performed with Cu(I) dissolved in PMDTA with same monomers, without using heteregenous CU(I)SNW catalyst, the obtained molecular weight of the polymer was about 150000 g/mol. It may be because of the pore size of our Cu(I)SNW polymer which may limit the polymerization. Further investigations will be performed on this situation.

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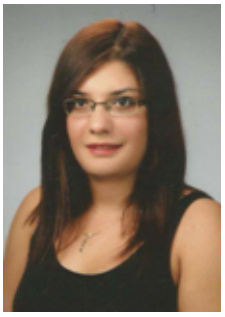

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